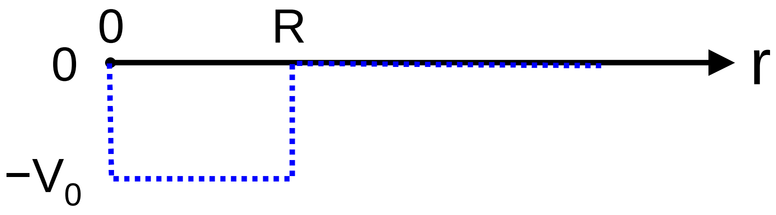
Solutions to Schrödinger's equation for spherical potential wells:

Modelling the Atomic Nucleus

and the H atom electron

1. Modelling the Atomic Nucleus

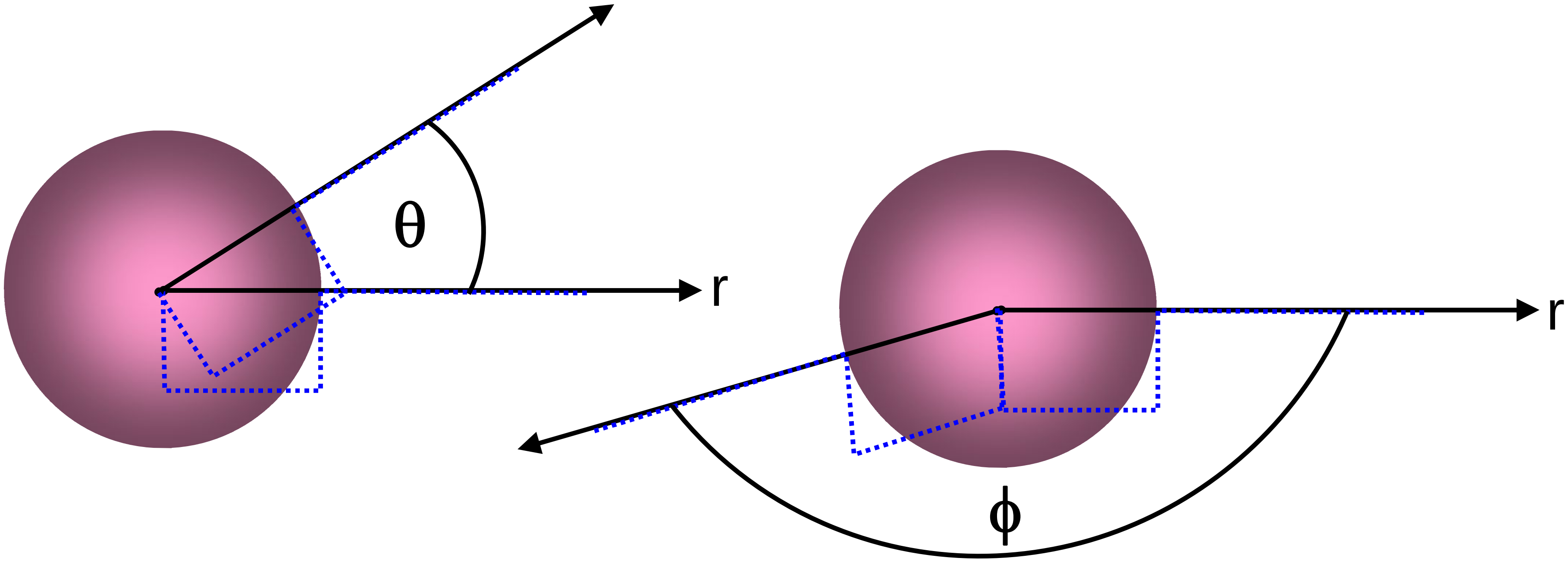
Using a spherical rectangular potential well



$V(r) = 0$ for $r \geq R$

$V(r) = -V_0$ for $r < R$

1D finite rectangular well



(3D) finite spherical rectangular well

We begin by using the time-independent Schrodinger wave equation (TISWE):

$$\left[\frac{\partial}{\partial x^2}+\frac{\partial}{\partial y^2}+\frac{\partial}{\partial z^2}\right]\psi+\frac{2M}{\hbar^2}\left[E-V(r)\right]\psi=0$$

Where:

M = nucleon mass, E = total energy of nucleon (= 0 at nuclear surface)
V(r) is the finite spherical rectangular well potential function:

V(r) = 0 for r ≥ R
V(r) = $-V_0$ for r < R

In spherical polars (changing the Laplacian operator):

x = rsinθsinϕ, y = rsinθsinϕ, z = rcosθ

The TISWE becomes:

$$\left[\frac{\partial}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}+\frac{1}{r^2}\frac{\partial}{\partial \theta^2}+\frac{\cot\theta}{r^2}\frac{\partial}{\partial\theta}+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi+\frac{2M}{\hbar^2}\left[E-V(r)\right]\psi=0$$

Separation of variables gives:

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$$

$$gives:$$

$$Y\frac{d^2}{dr^2} + \frac{2Y}{r}\frac{dR}{dr} + \frac{R}{r^2}\frac{\partial^2 Y}{\partial\theta^2} + \frac{\cot\theta}{r^2}R\frac{\partial Y}{\partial\theta} + \frac{R}{r^2\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2} + \frac{2M}{\hbar^2}\left[E - V(r)\right]RY = 0$$

$$(\text{multiply by } \mathrm{r}^2/\mathrm{RY}):$$

$$\frac{r^2}{R}\frac{d^2R}{dr^2} + \frac{2r}{R}\frac{dR}{dr} + \frac{2Mr^2}{\hbar^2}\left[E - V(r)\right] = -\frac{1}{Y}\left[\frac{\partial^2 Y}{\partial\theta^2} + \cot\theta\frac{\partial Y}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right] = l(l+1)$$

Where we have set each side equal to a constant which we have designated l(l+1) for later convenience.

$$\frac{r^2}{R}\frac{d^2R}{dr^2} + \frac{2r}{R}\frac{dR}{dr} + \frac{2Mr^2}{\hbar^2}\left[E - V(r)\right] = l(l+1) \qquad (1)$$

$$\frac{1}{Y}\left[\frac{\partial^2 Y}{\partial\theta^2} + \cot\theta\frac{\partial Y}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right] + l(l+1) = 0 \qquad (2)$$

Separating Y further by variables gives:

$$Y(\theta,\phi) = \Theta(\theta)\Phi(\phi)$$

$$gives \text{ (in equation 2)}$$

$$\frac{1}{\Theta\Phi}\left[\Phi\frac{d^2\Theta}{d\theta^2} + \Phi\cot\theta\frac{d\Theta}{d\theta} + l(l+1)\right] = -\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = m^2$$

where we have set each side equal to a constant designated m^2

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -m^2$$ (3, m is zero or a positive integer)

$$\frac{1}{\Theta}\frac{d^2\Theta}{d\theta^2} + \frac{1}{\Theta}\cot\theta\frac{d\Theta}{d\theta} + l(l+1) - \frac{m^2}{\sin^2\theta} = 0$$ (4)

Equation 3 is for the familiar harmonic oscillator whose solution is:

$$\Phi(\phi) = Ae^{i(m\phi+B)} = A(\cos(m\phi + B) + i\sin(m\phi + B))$$

The solution to equation 4:

$$\frac{1}{\Theta}\frac{d^2\Theta}{d\theta^2}+\frac{1}{\Theta}\cot\theta\frac{d\Theta}{d\theta}+l(l+1)-\frac{m^2}{\sin^2\theta}=0$$

Change of variable, let $\mu = \cos\theta$, gives:

$$d\mu/d\theta=-\sin\theta$$

$$d^2\mu/d\theta^2=-\cos\theta$$

Chain rule :

$$\frac{\mathrm{d}}{\mathrm{d}\mu}=\frac{d\theta}{d\mu}\frac{d}{d\theta}$$

$$\frac{d}{d\theta}=\frac{d\mu}{d\theta}\frac{d}{d\mu}=-\sin\theta\frac{d}{d\mu}$$

$$\frac{d}{d\theta}\left(\frac{d\Theta}{d\theta}\right)=\frac{d}{d\theta}\left(-\sin\theta\frac{d\Theta}{d\mu}\right)=-\cos\theta\frac{d\Theta}{d\mu}-\sin\theta\frac{d}{d\theta}\frac{d\Theta}{d\mu}$$

$$-\cos\theta\frac{d\Theta}{d\mu}-\sin\theta\frac{d}{d\theta}\frac{d\Theta}{d\mu}=-\cos\theta\frac{d\Theta}{d\mu}+\sin^2\theta\frac{d}{d\mu}\frac{d\Theta}{d\mu}$$

gives

$$\frac{d^2\Theta}{d\theta^2}=(1-\mu^2)\frac{d^2\Theta}{d\mu^2}-\mu\frac{d\Theta}{d\mu}$$

Substituting in d/dθ and $d^2/d\theta^2$ in terms of μ :

$$\frac{d^2\Theta}{d\theta^2}+\cot\theta\frac{d\Theta}{d\theta}+\left(l(l+1)-\frac{m^2}{\sin^2\theta}\right)\Theta=0$$

gives

$$\left(1-\mu^2\right)\frac{d^2\Theta}{d\mu^2}-2\mu\frac{d\Theta}{d\mu}+\left(l(l+1)-\frac{m^2}{\sin^2\theta}\right)\Theta=0$$

Considering the simplest case where m = 0, gives:

$$\left(1-\mu^2\right)\frac{d^2\Theta}{d\mu^2} - 2\mu\frac{d\Theta}{d\mu} + l(l+1)\Theta = 0$$

This is **Legendre's equation**!

This can be solved by power series solution. The solutions are Legendre polynomials, $P_l(\mu) = P_l(\cos\theta)$, the first few of which are:

$$P_0(\cos\theta) = 1$$

$$P_1(\cos\theta) = \cos\theta$$

$$P_2(\cos\theta) = \frac{1}{2}(3\cos^2\theta - 1)$$

$$P_3(\cos\theta) = \frac{1}{2}(5\cos^3\theta - 3\cos\theta)$$

$$P_4(\cos\theta) = \frac{1}{8}(35\cos^4\theta - 30\cos^2\theta + 3)$$

For the general case, including m ≠ 0, and as long as |m| ≤ l, a solution which remains finite for all values of μ is:

$$P_l^m(\mu) = (1-\mu^2)^{|m|/2} \frac{d^{|m|}}{d\mu^{|m|}} P_l(\mu)$$

where $P_l^m(\mu)$ is the **associated Legendre function**.

The associated Legendre function multiplied by the solution to equation 3 for ϕ, and normalised, gives the **spherical harmonics** which are solutions to $Y(\theta,\phi) = \Theta(\theta)\Phi(\phi)$:

$$Y_l^m(\theta,\phi) = \sqrt{\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}} \cdot P_l^m(\cos\theta)e^{im\phi}$$

Associated Legendre Functions with argument cosθ

$$P_0^0(\cos\theta) = 1$$

$$P_1^0(\cos\theta) = \cos\theta$$

$$P_1^1(\cos\theta) = -\sin\theta$$

$$P_2^0(\cos\theta) = \frac{1}{2}(3\cos^2\theta - 1)$$

$$P_2^1(\cos\theta) = -3\sin\theta\cos\theta$$

$$P_2^2(\cos\theta) = 3\sin^2\theta$$

$$P_3^0(\cos\theta) = \frac{1}{2}\cos\theta(5\cos^2\theta - 3)$$

$$P_3^1(\cos\theta) = -\frac{3}{2}(5\cos^2\theta - 1)\sin\theta$$

$$P_3^2(\cos\theta) = 15\cos\theta\sin^2\theta$$

$$P_3^3(\cos\theta) = -15\sin^3\theta$$

Spherical Harmonics

$$Y_l^m(\theta,\phi) = \sqrt{\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}} \cdot P_l^m(\cos\theta)e^{im\phi}$$

$$Y_l^m(\theta,\phi)$$

$$Y_0^0(\theta,\phi) = \frac{1}{2}\frac{1}{\sqrt{\pi}}$$

$$Y_1^0(\theta,\phi) = \frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$$

$$Y_1^1(\theta,\phi) = -\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{-i\phi}$$

$$Y_2^0(\theta,\phi) = \frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta - 1)$$

$$Y_2^1(\theta,\phi) = -\frac{1}{2}\sqrt{\frac{15}{2\pi}}\sin\theta\cos\theta e^{i\phi}$$

$$Y_2^2(\theta,\phi) = \frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta e^{2i\phi}$$

$$Y_3^0(\theta,\phi) = \frac{1}{4}\sqrt{\frac{7}{\pi}}(5\cos^3\theta - 3\cos\theta)$$

$$Y_3^1(\theta,\phi) = -\frac{1}{8}\sqrt{\frac{21}{\pi}}\sin\theta(5\cos^2\theta - 1)e^{i\phi}$$

$$Y_3^2(\theta,\phi) = \frac{1}{4}\sqrt{\frac{105}{2\pi}}\sin^2\theta\cos\theta e^{2i\phi}$$

$$Y_3^3(\theta,\phi) = -\frac{1}{8}\sqrt{\frac{35}{\pi}}\sin^3\theta e^{3i\phi}$$

Returning to the radial equation (1):

$$\frac{r^2}{R}\frac{d^2R}{dr^2}+\frac{2r}{R}\frac{dR}{dr}+\frac{2Mr^2}{\hbar^2}\left[E-V(r)\right]=l(l+1)$$

We introduce the wave number:

$$k^2=[E-V(r)]\,2M\big/\hbar^2$$

and change the variable to ρ = kr and replace R by $\sqrt{(\pi/2kr)}R'$

$$d\rho\big/dr=k,\ \ r=\rho/k$$

$$\text{chain rule:}$$

$$\frac{dR}{dr}=\frac{dR}{d\rho}\frac{d\rho}{dr}=k\frac{dR}{d\rho}$$

$$\frac{d^2R}{dr^2}=k\frac{d}{dr}\left(\frac{dR}{d\rho}\right)=k^2\frac{d}{d\rho}\left(\frac{dR}{d\rho}\right)=k^2\frac{d^2R}{d\rho^2}$$

gives

$$\frac{\rho^2}{R}\frac{d^2R}{d\rho^2}+\frac{2\rho}{R}\frac{dR}{d\rho}+\rho^2-l(l+1)=0$$

with

$$R=\sqrt{\frac{\pi}{2kr}}R'=\sqrt{\frac{\pi}{2\rho}}R'$$

$$\frac{dR}{d\rho}=-\frac{1}{2}\sqrt{\frac{\pi}{2}}\rho^{-3/2}R'+\sqrt{\frac{\pi}{2}}\rho^{-1/2}\frac{dR'}{d\rho}$$

$$\frac{d^2R}{d\rho^2}=\frac{3}{4}\sqrt{\frac{\pi}{2}}\rho^{-5/2}R'-\frac{1}{2}\sqrt{\frac{\pi}{2}}\rho^{-3/2}\frac{dR'}{d\rho}-\frac{1}{2}\sqrt{\frac{\pi}{2}}\rho^{-3/2}\frac{dR'}{d\rho}+\sqrt{\frac{\pi}{2}}\rho^{-1/2}\frac{d^2R'}{d\rho^2}$$

Substituting in the new expressions for our differential operators into:

$$\frac{\rho^2}{R}\frac{d^2R}{d\rho^2}+\frac{2\rho}{R}\frac{dR}{d\rho}+\rho^2-l(l+1)=0$$

gives

$$\rho^2\left(\frac{3}{4}\sqrt{\frac{\pi}{2}}\rho^{-5/2}R'-\sqrt{\frac{\pi}{2}}\rho^{-3/2}\frac{dR'}{d\rho}+\sqrt{\frac{\pi}{2}}\rho^{-1/2}\frac{d^2R'}{d\rho^2}\right)$$

$$+2\rho\left(-\frac{1}{2}\sqrt{\frac{\pi}{2}}\rho^{-3/2}R'+\sqrt{\frac{\pi}{2}}\rho^{-1/2}\frac{dR'}{d\rho}\right)+\left(\rho^2-l(l+1)\right)\sqrt{\frac{\rho}{2}}\rho^{-1/2}R'$$

gives

$$\frac{3}{4}\rho^{-1/2}R'-\rho^{1/2}\frac{dR'}{d\rho}+\rho^{3/2}\frac{d^2R'}{d\rho^2}-\rho^{-1/2}R'+2\rho^{1/2}\frac{dR'}{d\rho}+(\rho^2-l(l+1))\rho^{-1/2}R'$$

gives

$$\rho^{3/2}\frac{d^2R'}{d\rho^2}+\rho^{1/2}\frac{dR'}{d\rho}+\frac{1}{4}\rho^{-1/2}R'+(\rho^2-l(l+1))\rho^{-1/2}R'$$

gives

$$\rho^2 \frac{d^2R'}{d\rho^2} + \rho \frac{dR'}{d\rho} - \frac{1}{4}R' + (\rho^2 - l(l+1))\rho^{-1/2}R'$$

since

$$\left(l + \frac{1}{2}\right)^2 = \left(l + \frac{1}{2}\right)\left(l + \frac{1}{2}\right) = l^2 + l + \frac{1}{4} = l(l+1) + \frac{1}{4}$$

we have

$$\boxed{\rho^2 \frac{d^2R'}{d\rho^2} + \rho \frac{dR'}{d\rho} + \left(\rho^2 - \left(l + \frac{1}{2}\right)^2\right)R' - 0}$$

which is Bessel's equation!

Solutions to Bessel's equation:

$$\rho^2 \frac{d^2R'}{d\rho^2} + \rho \frac{dR'}{d\rho} + \left(\rho^2 - \left(l + \frac{1}{2} \right)^2 \right) R' - 0$$

for half an odd integer, $J_{l+½}$, are:

$$R(r) = j_l(kr) = \sqrt{\frac{\pi}{2kr}} \cdot J_{l+1/2}(kr)$$

which are **<u>spherical Bessel functions</u>**, the first few of which are:

$$j_0(kr) = \frac{1}{kr} \sin kr$$

$$j_1(kr) = \frac{1}{(kr)^2} \sin kr - \frac{1}{kr} \cos kr$$

Higher order solutions can be found from the recurrence formula:

$$j_{l+1}(kr) = \frac{2l+1}{kr} j_l(kr) - j_{l-1}(kr)$$

Energy Eigenvalues

Consider the first solution for l = 0:

$$R(r) = j_0(kr) = \frac{\sin kr}{kr}$$

This must be zero at the nuclear surface (boundary condition) requiring :

$$\frac{\sin kR_{nuc}}{kR_{nuc}} = 0$$

where $r = R_{nuc}$ is the nuclear radius

The smallest value of k satisfying this condition is :

$$kR_{nuc} = k_{10}R_{nuc} = \pi$$

The next smallest is (l still zero) :

$$k_{20}R_{nuc} = 2\pi$$

Where we have introduced two quantum umbers, ν and l :

$$\frac{\hbar^2 k_{\nu l}^2}{2M} = [E_{\nu l}^{tot} - V(r)] = E_\nu$$

Gives the kinetic energy of each eigenfunction designated by E_ν with :

$$\nu = 1, 2, 3, \ldots$$

Evaluation of the model

If we construct a nucleus by assuming that neutrons and protons can populate the same set of energy levels (requiring that no two neutrons or protons can have the same set of quantum numbers and introducing nucleon spin with two possible values: +½ and −½) we predict the first few **magic numbers**, corresponding to fully occupied energy levels (ν): 2, 8 and 20. However, it fails to accurately predict the higher magic numbers given by the **shell model**.

Our rectangular spherical potential, in which the potential abruptly changes at the nuclear surface, is inaccurate. A more realistic potential would include a more gradual change in potential at the well edge (such as by using the Woods-Saxon potential). We also need to account for fine structure by introducing **spin-orbit coupling**.

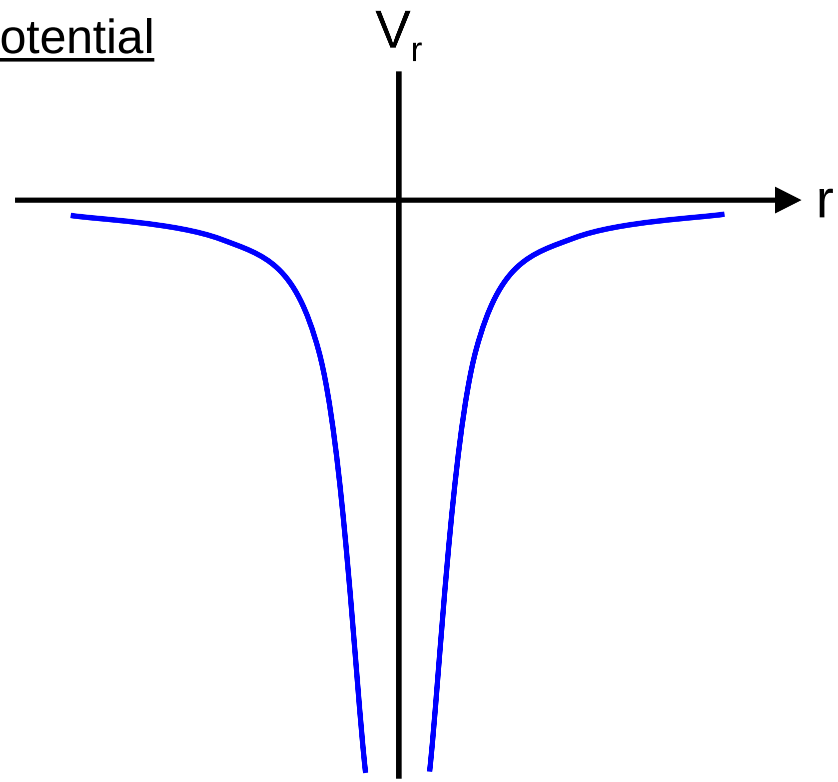
the introduction of spin-orbit coupling accurately predicts all the magic numbers (at least up to 184). The shape of the well (flatness of the well bottom and the steepness of its sides) affects the exact energy levels, but not their order (again we reserve the possibility of differences for very high magic numbers).

2. Modelling the Hydrogen Atom Using a Coulomb Potential Well

The **Coulomb potential** is a central (spherically symmetric) potential and the angular part of the wave functions are the same as for any other central potential, namely the spherical harmonics.

However, the radial wavefunction is quite different from that for the spherical rectangular well.

The Coulomb potential



$$\frac{r^2}{R}\frac{d^2R}{dr^2}+\frac{2r}{R}\frac{dR}{dr}+\frac{2Mr^2}{\hbar^2}\left[E-V(r)\right]=l(l+1)$$

Change of variable : let G(r) = rR(r) :

$$\frac{\mathrm{d}}{\mathrm{dr}}(rR(r)) = R(r)+r\frac{dR(r)}{dr}$$

$$\frac{d^2G(r)}{dr^2}=\frac{\mathrm{d}^2}{\mathrm{dr}^2}(rR(r)) = \frac{d}{dr}\left[R(r)+r\frac{dR(r)}{dr}\right]$$

$$=\frac{dR}{dr}+\frac{dR}{dr}+r\frac{d^2r}{dr^2}=r\frac{d^2r}{dr^2}+2\frac{dR}{dr}$$

Gives :

$$\frac{r^2}{G}\frac{d^2G}{dr^2}+\frac{2Mr^2}{\hbar^2}[E-V(r)]-l(l+1)=0$$

with

$$V(r)=-\frac{e^2}{r}, \text{(in cgs units), or : } V(r)=-\frac{e^2}{4\pi\varepsilon_0 r}, \text{(in SI units)}$$

This gives :

$$\frac{d^2G}{dr^2}+\frac{2M}{\hbar^2}\left[E+\frac{e^2}{r}-\frac{l(l+1)\hbar^2}{2Mr^2}\right]G=0$$

which is equivalent to :

$$\left[-\frac{\hbar^2}{2M}\frac{d^2}{dr^2}+\frac{l(l+1)\hbar^2}{2Mr^2}-\frac{e^2}{r}\right]G=EG$$

Using the natural units :

$\rho=\dfrac{r}{a_0}$, where a_0 is the Bohr radius

$$\varepsilon=\frac{E}{E_R}$$

we have

$$r=a_0\rho=\frac{\hbar^2}{Me^2}\rho$$

$$E = E_R\varepsilon = \frac{Me^4}{2\hbar^2}\varepsilon$$

which gives :

$$\left[-\frac{\mathrm{Me}^4}{2\hbar^2}\frac{d^2}{d\rho^2} + \frac{\mathrm{Me}^4}{2\hbar^2\rho^2}l(l+1) - \frac{Me^2}{\hbar^2\rho}e^2\right]G = \frac{\mathrm{Me}^4}{2\hbar^2}\varepsilon G$$

i.e.

$$\left[-\frac{d^2}{d\rho^2} + \frac{l(l+1)}{\rho^2} - \frac{2}{\rho}\right]G = \varepsilon G$$

gives :

$$-\frac{d^2G}{d\rho^2} + V_{eff}G = \varepsilon G$$

where the effective potential is (in natural units) :

$$V_{eff}(\rho) = \frac{l(l+1)}{\rho^2} - \frac{2}{\rho}$$

or, in ergs :

$$V_{eff}(\rho) = \frac{l(l+1)}{2Mr^2} - \frac{e^2}{r}$$

Where the first term on the RHS is the centrifugal potential, $l(l+1)/2Mr^2$, and the second term is the coulomb energy, $-e^2/r$.

Let's consider limiting cases:

$$for\ \rho \to \infty, \text{ the Coulomb energy} \to 0 \text{ and}$$

$$l(l+1)\big/2Mr^2 \to 0$$

which gives :

$$\frac{d^2G}{d\rho^2} \approx -\varepsilon G$$

For bound states $E < 0$ and so $-\varepsilon > 0$, so :

$$\frac{d^2G}{d\rho^2} + \varepsilon G = 0$$

An acceptable solution to this equation is :

$$G(\rho) \sim e^{-b\rho}$$

where $\varepsilon = -b^2, b \geq 0$

As can be seen by substituting this solution back into the DE :

$$\frac{dG}{d\rho} = -be^{-b\rho}$$

$$\frac{d^2G}{d\rho^2} = b^2e^{-b\rho} = -\varepsilon G$$

At the other extreme, when $\rho \to 0$ we have:

$$\frac{d^2G}{d\rho^2} \approx \frac{l(l+1)}{\rho^2} G$$

An acceptable solution of which is :

$$G(\rho) \sim \rho^{l+1}$$

$$\frac{dG}{d\rho} \approx (l+1)\rho^{l}$$

$$\frac{d^2G}{d\rho^2} \approx l(l+1)\rho^{l-1} = \frac{l(l+1)}{\rho^2} \rho^{l+1}$$

Therefore, we expect the solution to be of the form :

$$\mathrm{G}(\rho) \sim \rho^{l+1} e^{-b\rho}$$

The general solution is expected to be this solution multiplied by a polynomial :

$$G(\rho) = \rho^{l+1} e^{-b\rho} \sum_{i=o}^{i_{\max}} (-1)^i c_i \rho^i$$

To see this : consider the wave nature of the bound states with alternating parity.

We shall see shortly that b = 1/n, so we have :

$$G(\rho) = \rho^{l+1} e^{-\rho/n} \sum_{i=o}^{i_{\max}} (-1)^i c_i \rho^i = \rho^{l+1} e^{-\rho/n} f(\rho)$$

Now we need to find the values of the coefficients, c_i:

If G(ρ) satisfies :

$$\left[-\frac{d^2}{d\rho^2} + \frac{l(l+1)}{\rho^2} - \frac{2}{\rho} \right] G = \varepsilon G \Rightarrow \frac{d^2 G}{d\rho^2} = \left(\frac{l(l+1)}{\rho^2} - \frac{2}{\rho} - \varepsilon \right) \rho^{l+1} e^{-b\rho} f$$

then it can be shown that f(ρ) satisfies :

$$\frac{\rho d^2 f}{d\rho^2} + 2[(l+1) - b\rho] \frac{df}{d\rho} + 2[1 - b(l+1)] f = 0$$

as follows :

$$\frac{\mathrm{dG}}{d\rho} = (l+1)\rho^l e^{-b\rho} f - b\rho^{l+1} e^{-b\rho} f + p^{l+1} e^{-b\rho} \frac{df}{d\rho}$$

$$\frac{d^2 G}{d\rho^2} = \left(\frac{l(l+1)}{\rho^2} - \frac{2b(l+1)}{\rho} + b^2 \right) \rho^{l+1} e^{-b\rho} f + 2\left(\frac{l(l+1)}{\rho} - b \right) p^{l+1} e^{-b\rho} \frac{df}{d\rho} + p^{l+1} e^{-b\rho} \frac{d^2 f}{d\rho^2}$$

Thus :

$$\left(\frac{l(l+1)}{\rho^2}-\frac{2b(l+1)}{\rho}+b^2\right)f+2\left(\frac{l(l+1)}{\rho}-b\right)\frac{df}{d\rho}+\frac{d^2f}{d\rho^2}=\left(\frac{l(l+1)}{\rho^2}-\frac{2}{\rho}-\varepsilon\right)f$$

$$\Rightarrow$$

$$\rho\frac{d^2f}{d\rho^2}+2\big(l(l+1)-b\rho\big)\frac{df}{d\rho}+2\big(1+\varepsilon\rho-b(l+1)+\rho b^2\big)f$$

$$\Rightarrow$$

$$\rho\frac{d^2f}{d\rho^2}+2\big(l(l+1)-b\rho\big)\frac{df}{d\rho}+2\big(1-b(l+1)\big)f$$

as required (since $\varepsilon = -b^2$).

The equation :

$$\rho \frac{d^2 f}{d\rho^2} + 2[(l+1) - b\rho]\frac{df}{d\rho} + 2[1 - b(l+1)]f = 0$$

is very similar to Laguerre's differential equation into which it can be transformed by a suitable change of variable. The polynomial solutions we seek, f, will turn out to be solutions to Laguerre's equation, called Laguerre poynomials.

Rearranging for later convenience :

$$\rho \frac{d^2 f}{d\rho^2} + 2(l+1)\frac{df}{d\rho} = 2b\rho \frac{df}{d\rho} + 2[b(l+1) - 1]f = 0$$

and substituting in f and using the fact that the number of modes

for stationary waves = n - l - 1 :

$$\frac{\mathrm{d}}{\mathrm{d}\rho}\sum_{i=0}^{n-l-1}(-1)^{\mathrm{i}} c_i \rho^i = \sum_{i=0}^{n-l-1}(-1)^{\mathrm{i}} c_i i \rho^{i-1}$$

$$\frac{d^2 f}{d\rho^2} = \sum_{i=0}^{n-l-1}(-1)^{\mathrm{i}} c_i (i-1) i \rho^{i-2}$$

$$\Rightarrow$$

$$\sum_{i=0}^{n-l-1}(-1)^{\mathrm{j}}c_i(i-1)i\rho^{i-1}+2(l+1)\sum_{i=0}^{n-l-1}(-1)^{\mathrm{i}}c_i\rho^{i-1}=2b\sum_{i=0}^{n-l-1}(-1)^{\mathrm{i}}c_i i\rho^{i}+2[b(l+1)-1]\sum_{i=0}^{n-l-1}(-1)^{\mathrm{i}}c_i\rho^{i}$$

$$\Rightarrow\sum_{i=0}^{n-l-1}(-1)^{\mathrm{i}}c_i[(i-1)i+2(l+1)i]\rho^{i-1}=\sum_{i=0}^{n-l-1}(-1)^{\mathrm{j}}c_i[2bi+2(b(l+1)-1)]\rho^{i}$$

Thus :

$$\sum_{i=0}^{n-l-1}(-1)^{\mathrm{j}}c_j[(j-1)j+2(l+1)j]\rho^{j-1}=\sum_{i=0}^{n-l-1}(-1)^{\mathrm{j}}c_i[2bi+2(b(l+1)-1)]\rho^{i}$$

When j = 1 + 1, we have:

$$[i(i+1)+2(l+1)(i+1)]c_{i+1}=-[2bi+2(b(l+1)-1)]c_i$$

each term must separately equal zero and with $i = n\text{-}l\text{-}1$, we have :

$$0=-[2\mathrm{b}(\mathrm{n}-\mathrm{l}-1)+2(\mathrm{b}(\mathrm{l}+1)-1)]\mathrm{c}_{\mathrm{n\text{-}l\text{-}1}}$$

which gives $\mathrm{b}=1/\mathrm{n}$

Now we have a formula for the coefficients :

$$\frac{\mathrm{c}_{\mathrm{i}+1}}{\mathrm{c}_{\mathrm{i}}}=\frac{2(n-l-1-i)}{n(i+1)(2l+2+i)}$$

Energy eigenvalues

Referring back to our equation for E:

$$E = E_R \varepsilon = \frac{Me^4}{2\hbar^2}\varepsilon$$

Since we know that $\varepsilon = -b^2$ and b = 1/n, we have the equation for the energy eigenvalues, one eigenvalue corresponding to each orbital:

$$E_n = -\frac{Me^4}{2\hbar^2 n^2} \text{ (cgs units)}$$

$$E_n = -\frac{Me^4}{2\hbar^2 n^2}\left(\frac{\mathrm{e}^2}{4\pi\varepsilon_0}\right) \text{ (SI units)}$$

$$n = 1, 2, 3, \ldots$$

The negative sign indicates bound states. (Fine and hyperfine structure corrections can be applied to E_n for more accuracy).

<u>Normalisation</u>

We still need to determine the coefficient c_0 which will enable us to determine the other coefficients by recursion. To determine c_0 we require the integral of the square of the wavefunction = 1, since this is the probability distribution function of the electron and the probability of the electron being somewhere in space = 1.

$$\int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\left|\psi_{nlm}(r,\theta,\phi)\right|^2 r^2 \sin\theta dr d\theta d\phi = 1$$

$$a_0^3\int_{r=0}^{\infty}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\left|\rho^l e^{-\rho/n} f_{nl}(\rho) Y_{lm}(\theta,\phi)\right|^2 \rho^2 \sin\theta d\rho d\theta d\phi = 1$$

With Y_{lm} normalised:

$$\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\left|Y_{lm}(\theta,\phi)\right|^2 \sin\theta d\theta d\phi = 1$$

we require:

$$\mathrm{a}_\mathrm{o}^3\int_0^{\infty}\rho^{2l+2}\left|f_{nl}(\rho)\right|^2 e^{-2\rho/n} dp = 1$$

$\mathrm{f}_{nl}(\rho)$ is normalised when c_0 is, e.g.

for $l = 0$, $\mathrm{n} = 1$:

$$\mathrm{a}_\mathrm{o}^3\int_0^{\infty}\rho^{2l+2}\left|c_0\right|^2 e^{-2\rho/n} dp = 1$$

Using the following standard integral :

$$\int_0^{\infty} \mathrm{r}^{\mathrm{q}} e^{-\alpha r} dr = \frac{q!}{\alpha^{q+1}}$$

We obtain :

$$| c_0 |^2 = \frac{2^2}{a_0^3}$$

gives :

$$| c_0 | = 2a_0^{-3/2}$$

Note : the sign of c_0 is unimportant since we square the wavefunction to obtain the observable probability distribution.

Some radial wavefunctions, $R_{nl}(r)$:

$$R_{10} = 2\left(\frac{1}{a_0}\right)^{\frac{3}{2}} e^{-r/a_0}$$

$$R_{20} = 2\left(\frac{1}{2a_0}\right)^{\frac{3}{2}}\left(1-\frac{r}{2a_0}\right)e^{-r/2a_0}$$

$$R_{21} = \frac{1}{\sqrt{3}}\left(\frac{1}{2a_0}\right)^{\frac{3}{2}}\left(\frac{r}{a_0}\right)e^{-r/2a_0}$$

$$R_{30} = 2\left(\frac{1}{3a_0}\right)^{\frac{3}{2}}\left(1-\frac{2r}{3a_0}+\frac{2r^2}{27a_0^2}\right)e^{-r/3a_0}$$

$$R_{31} = \frac{4\sqrt{2}}{3}\left(\frac{1}{3a_0}\right)^{\frac{3}{2}}\left(\frac{r}{a_0}\right)\left(1-\frac{r}{6a_0}\right)e^{-r/3a_0}$$

$$R_{32} = \frac{2\sqrt{2}}{27\sqrt{5}}\left(\frac{1}{3a_0}\right)^{\frac{3}{2}}\left(\frac{r}{a_0}\right)^2 e^{-r/3a_0}$$

Putting it all together

Radial wave functions

$$R_{nl} = N_{nl}\left(\frac{2r}{na_0}\right)^l e^{-r/na_0} L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right)$$

$n = 1, 2, 3, \ldots, \quad l = 0, 1, 2, \ldots, n - 1$

Note : $2r/na_0$ is the argument of the Laguerre polynomials

The radial normalisation coefficient is given by :

$$N_{nl} = \frac{1}{a_0^{3/2}}\frac{2}{n^2}\sqrt{\frac{(n-l-1)!}{(n+l)!}}$$

Laguerre polynomials :

$$L_p^k(x) = \sum_{s=0}^{p}(-1)^s \binom{p+k}{p-s}\frac{x^s}{s!}$$

For example :

$$L_0^k(x) = 1$$

$$L_1^k(x) = -x + k + 1$$

$$L_2^k(x) = \frac{1}{2}\left[x^2 - 2(k+2)x + (k+1)(k+2)\right]$$

$$L_3^k(x) = \frac{1}{6}\left[-x^3 + 3(k+3)x^2 - 3(k+2)(k+3)x + (k+1)(k+2)(k+3)\right]$$

E.g.

1s orbital :

$$Y_0^0 = \frac{1}{2\sqrt{\pi}}$$

$$\psi_{100}(r) = e^{-r/a_0}\,\frac{2a_0^{-3/2}}{2\sqrt{\pi}}$$

4f orbital with m = 1 :

$$\psi_{431}(r) = -\frac{1}{a_0^{3/2}}\frac{1}{8}\sqrt{\frac{1}{7!}}\left(\frac{r}{2a_0}\right)^3 e^{-r/4a_0}\,\frac{1}{8}\sqrt{\frac{21}{\pi}}\sin\theta(5\cos^2\theta-1)e^{i\phi}$$